# Saturation, Reduction, and the Formation of Iron-Manganese Concretions in the Jackson-Frazier Wetland, Oregon

David V. D'Amore,\* Scott R. Stewart, and J. Herbert Huddleston

#### **ABSTRACT**

The Jackson-Frazier wetland is a rare, relatively undisturbed wetland in the Willamette Valley of Oregon that experiences repetitive annual flooding and drying cycles. Redoximorphic features formed by these wetting and drying cycles have not been calibrated with saturation and reduction. Long-term measurements of soil saturation and soil redox potential (E<sub>H</sub>) were combined with measurements of Fe and Mn concentrations to understand the formation of these redoximorphic features in the wetland soils. The Jackson-Frazier wetland is underlain by three stratigraphic units that control its hydrology: Holocene alluvium (A and Bss horizons), Malpass clay (2Bt horizon), and Irish Bend silts (3BC horizon). All three units are saturated for up to 9 mo each year, leading to E<sub>H</sub> values that fall below the Fe reduction threshold. Extractable Fe and Mn in nodules, concretions, and soft masses document substantial depletions from the matrix soil in all three units. In the 3BC, diffuse halos of Fe accumulation and matrix chromas from two to four indicate a source of Fe that can be reduced, translocated, and concentrated in nodular form. In the Bss and 3BC horizons, soft masses surrounding concentrations and higher ratios of oxalate to dithionite-citrate-bicarbonate Fe ( $Fe_{Ox}/Fe_{DCB}$ ) in the larger concentrations suggest that nodules and concretions are currently forming by accretion of Fe. In the 2Bt, virtually all of the Fe and Mn is gone from the matrix, and concretion boundaries are sharp. These are not relict features, as the current conditions would favor continued formation had the supply of Fe and Mn not been exhausted.

REDOXIMORPHIC FEATURES are used to identify hydric soils through detailed soil descriptions calibrated with field measurements (Hurt et al., 2002). Redoximorphic features can only be applied to the classification of soils after these features have been calibrated with local conditions of saturation and reduction through longterm measurements of hydrology and anaerobic conditions in soils (Vepraskas and Sprecher, 1997). Verification of the connection between the formation of redoximorphic features and hydrologic and chemical processes has become the focus for many soil studies (Faulkner et al., 1989; Cogger and Kennedy, 1992; Megonigal et al., 1993; Wakeley et al., 1996). Understanding the formation of redoximorphic features is also important in deciphering the biogeochemical, hydrologic, and/or climatic history of an area (Bouma, 1983; Moorman and van de Wetering, 1985; Vepraskas, 1994). Therefore, the complete characterization of wetland soils and associated

D.V. D'Amore, USDA Forest Service, Pacific Northwest Research Station, 2770 Sherwood Lane, Suite 2A, Juneau, AK 99801; S.R. Stewart, L.C. Lee and Associates, Seattle, WA 98119; J.H. Huddleston, Dep. of Crop and Soil Sci., Oregon State Univ., Corvallis, OR 97331. Received 21 Apr. 2003. \*Corresponding author (ddamore@fs.fed.us).

Published in Soil Sci. Soc. Am. J. 68:1012–1022 (2004). © Soil Science Society of America 677 S. Segoe Rd., Madison, WI 53711 USA redoximorphic features is important for a clear understanding of reductimorphic processes.

The Jackson-Frazier wetland is a rare, relatively undisturbed wetland in the Willamette Valley of Oregon that experiences repetitive annual flooding and drying cycles and serves as a model for natural wetland conditions in the area. The development of hydric soils in the wetland is driven by the annual flooding, prolonged periods of soil saturation, abundant organic carbon, and mild temperatures that facilitate reductive dissolution and segregation of Fe and Mn into redoximorphic concentrations and/or depletions (Somera, 1967; Cogger and Kennedy, 1992; Lovely, 1993; Miller et al., 1993; Vepraskas, 1994). Three distinct stratigraphic units within the Jackson-Frazier wetland all contain Fe-Mn concentrations in the form of macroscopic concretions and nodules (Stewart, 1997). Similar concentrations were identified as early as 1940 by Drosdoff and Nikiforoff (1940), and more recent work by Somera (1967) and Seter and Baham (1994) has shown that the greatest amount of nodules occur in the wettest (poorly drained) soils of the hydrosequences they studied.

We have previously described the hydrology of the wetland in relation to its stratigraphy (D'Amore et al., 2000). In this paper we show how saturation and reduction patterns influence the development of Fe-Mn concretions and present evidence that these concentrations, despite having distinct, sharp boundaries that may suggest transport or relict features (Vepraskas, 1994), have formed in place under biogeochemical, hydrologic, and redox environments that are still in place today. Specific objectives were to (i) determine the timing and duration of both saturation and reduction and their influence on conditions conducive to the development of redoximorphic features in each of the stratigraphic units, and (ii) explain the effects of prolonged anaerobiosis on the presence, number, and properties of Fe-Mn concentrations found in each stratigraphic unit.

#### **MATERIALS AND METHODS**

#### **Site Description**

The Willamette Valley is a broad level plain in western Oregon that lies between the Cascade Mountains to the east and the Coast Range Mountains to the west. The Jackson-Frazier wetland is a 64-ha area located at the margin of the valley north of Corvallis at an elevation of approximately 66 m. Vegetation includes forest, shrub-scrub, and prairie palustrine plant communities (Marshall, 1985). Surface water enters the NW corner of the wetland just downstream from the conflu-

**Abbreviations:** DCB, dithionite-citrate-bicarbonate; DO, dissolved oxygen;  $E_{H}$ , redox potential;  $Fe_{DCB}$ , dithionite-citrate-bicarbonate iron;  $Fe_{Ox}$ , acid ammonium oxalate iron;  $Mn_{DCB}$ , dithionite-citrate-bicarbonate manganese.

ence of Jackson and Frazier Creeks. Water exits the wetland both to the southeast via Stewart Slough and to the northeast via Frazier Creek ditch. Low relief and the presence of numerous beaver dams in the NW corner of the wetland have created complex, prolonged overland flow patterns and semipermanent saturation.

### Soils and Geomorphology

The geomorphic and stratigraphic setting of the Willamette valley has been discussed in detail by Reckendorf (1993). D'Amore et al. (2000) added details specific to the Jackson-Frazier wetland. Briefly stated, late Pleistocene episodic flooding of the valley associated with repeated failures of the ice dams that created glacial lake Missoula created a sequence of three distinct lacustrine sedimentary deposits, a thick buffcolored silty unit known as the Irish Bend silts (3BC horizon), a thin gray clayey unit called the Malpass clay (2Bt horizon), and a moderately thick surficial silty unit known as the Greenback silts. The Greenback member is not present in the Jackson-Frazier wetland, presumably because it was stripped away by very late Pleistocene or early Holocene erosion. Instead, the Malpass clay present in the wetland is overlain by clayey Holocene sediments (A and Bss horizons) that originated in the basaltic foothills immediately to the west and were deposited by Frazier Creek, forming a low alluvial fan that is thickest in the northwest corner and thins progressively to the southeast.

The soils of the wetland have formed in this sequence of sedimentary deposits. The surficial Holocene alluvium exhibits strong shrink-swell behavior, has well-formed slickensides, and is thick enough to control the classification of the soils throughout the wetland. Thus the Bashaw series, classified as very-fine, smectitic, mesic Xeric Endoaquerts (Soil Survey Division, 2003), is the soil of record. Piezometer data from 1992 to 1996 (D'Amore et al., 2000) show that the smectitic alluvium controls saturation and drying of the wetland surface, that the alluvium and the Malpass clay beneath it together act as an aquitard that restricts infiltration of surface water and limits recharge of underlying groundwater, and that there is a separate water table in the Irish Bend silts beneath the Malpass clay.

Soil, hydrologic, and redox data from two sites, labeled JF1 and JF2, are reported in this paper. Soil pits 2 by 1 by 2 m deep were hand dug at each site. Detailed morphological descriptions were made, and bulk samples adequate to provide large amounts of nodule and concretion-rich material were taken from Bss horizons in Holocene alluvium, the 2Bt horizon in Malpass clay, and the 3BC horizon in Irish Bend silts for further laboratory characterization.

# Field Instrumentation

Piezometers constructed from 1.9-cm o.d. schedule 20 PVC pipe were installed in triplicate at both sites at depths of 25, 50, and 100 cm. A single piezometer at the 200-cm depth also was installed at each site. Piezometric data were recorded weekly by measuring the depth from the ground surface to an indicator float.

Platinum electrodes similar to those of Faulkner et al. (1989) also were placed in triplicate at depths of 25, 50, and 100 cm at each site. Our electrodes, however, did not have a mercury junction. Instead, we soldered a copper wire lead directly onto the platinum tip and sealed the glass tube by filling it with epoxy. This provided both an insulated connection and an electrode with increased strength. Measurements of  $E_{\rm H}$  were made weekly with a voltmeter and a saturated calomel refer-

ence electrode. The average value of three measurements at each depth is reported as  $E_{\rm H}$  and has been adjusted to the standard hydrogen electrode by adding 244 mV to the raw voltmeter readings. Variability among the electrodes at each depth did not change the interpretation of the redox environment; therefore, we show only the average  $E_{\rm H}$  value at each depth. We have taken as our threshold for Fe reduction an  $E_{\rm H}$  of 200 mV based on relationships developed by Ponnamperuma (1972) at pH 7.

Soil temperature was measured by type K thermocouples, ungrounded and Iconel (International Nickel Co., Toronto, ON, Canada) sheathed. They were 1.2 m long and modified for field use by cutting to the desired length and fitting with male connectors for reading with a type K digital temperature gauge.

Dissolved oxygen (DO) in soil water was measured with an Orion 820 self-calibrating DO sensor (Orion Research, Inc., Boston, MA). The  $\rm O_2$  probe was lowered to the bottom of each piezometer and moved up and down gently to create flow of at least 1 cm s<sup>-1</sup> past the membrane until a stable value was reached. Piezometers were not pumped out before measurement because of the very slow refill time and the potential for aeration during refill.

#### **Laboratory Analyses**

#### **Concretions and Nodules**

Subsamples of the bulk soil samples were dried, weighed, and dispersed by shaking overnight in Na-hexametaphosphate. The combined sand and gravel fractions were then separated by wet sieving, dried, and weighed. Nodules and concretions were removed from the sand and gravel fraction by magnetic separation, and both their mass and volume were determined. Concretion or nodule densities were determined by weighing, coating with liquid Saran (Dow Chemical Co., Midland, MI), and measuring the volume of water displaced. Nodules and concretions were separated by sieving into a sand-sized (<2-mm) class and a gravel-sized (>2-mm) class before chemical analysis. Concretionary material in both classes was then ground gently into a fine powder.

# **Dithionite-Citrate-Bicarbonate Iron and Manganese**

Determinations of dithionite-citrate-bicarbonate-extractable Fe and Mn (Fe<sub>DCB</sub> and Mn<sub>DCB</sub>) were made on six samples per size class for Fe and four samples per size class for Mn, for both the powdered concretion and nodule material and the finely ground concretion- and nodule-free soil matrix. In both cases, fresh 50-mg samples were placed in 50-mL plastic centrifuge tubes. Five milliliters of deionized water and 5 mL of a 0.5 M citrate:0.2 M Na-bicarbonate stock were added to each tube. After placing tubes in a 75°C water bath for 5 min, approximately 0.33 g of sodium hydrosulfite was added to each tube. Tubes were shaken for 30 min, then centrifuged at 3000 rpm (1086  $\times$  g) for 20 min. The supernatant was decanted into 50-mL flasks. This procedure was repeated two additional times on the same samples.

Extracted Fe and Mn were analyzed after the method of Jackson et al. (1986) by placing 0.15 mL of sample in 5.1 mL of nanopure water, 0.25 mL of 2% hydroxylamine hydrochloride, 0.25 mL of 1.0 M sodium acetate/acetic acid buffer, and 0.25 mL of 0.4% 1,10 phenanthroline. The samples were mixed and set aside for at least 0.5 h before being analyzed in a Hewlett-Packard (Palo Alto, CA) 8453 UV visible spectrophotometer. Standards were made in the linear working range of 0 to 2.5 mg kg $^{-1}$  from a 50-mg kg $^{-1}$  stock solution of ferrous ammonium sulfate hexahydrate. The Fe<sub>DCB</sub> samples were air-

Table 1. Rainfall needed to bring soil to saturation and lag times to reduce iron after saturation at sites JF1 and JF2.

				JF1	JF2		
Depth	Year	Annual rainfall	Rainfall needed to saturate soil	Time after saturation to reduce soil Fe†	Rainfall needed to saturate soil	Time after saturation to reduce soil Fe†	
cm			- cm ———	d	cm	d	
25	1992	85	10.7	14	8.9	19	
	1993	91	5.3	15	3.4	6	
	1995	138	8.0	0	8.0	0	
	1996	186	12.3	0	12.3	0	
50	1992	85	10.7	14	8.9	26	
	1993	91	5.3	91	3.4	29	
	1995	138	8.0	0	8.0	0	
	1996	186	12.3	0	12.3	0	
100	1992	85	10.7	64	37.0	124	
	1993	91	25.1	NR	24.1	76	
	1995	138	8.0	0	8.0	6	
	1996	186	12.3	0	12.3	9	

<sup>†</sup> Time to reduce Fe is based on a threshold of 200 mV at pH 7.

bubbled for 2 h to oxidize the dithionite. The  $Mn_{\text{DCB}}$  was analyzed by atomic absorption analysis.

#### Acid Ammonium Oxalate Iron and Manganese

Fifty milligrams of ground material (soil matrix or concretions and nodules) were weighed into 50-mL centrifuge tubes. Ten milliliters of 0.2~M Fe $_{\rm Ox}$  were added to each tube in the absence of light. Tubes were shaken for 2.5 h and centrifuged at 1086~g for 0.5~h. The supernatant was decanted, diluted to 50~mL, and analyzed colorimetrically for Fe and Mn.

#### RESULTS AND DISCUSSION

#### **Conditions Conducive to Redox Processes**

Three conditions are necessary for the development of reducing conditions and redoximorphic features in soils: (i) saturation of sufficiently long duration to develop anaerobic soil, (ii) sufficient organic carbon and warm-enough soil temperatures to support soil microbial activity, and (iii) adequate supplies of Fe and Mn in the soil. Our data show that all of these conditions exist in the soils of the Jackson-Frazier wetland.

#### **Saturation and Anaerobiosis**

Data on the onset and duration of saturation at different depths in the soil are shown in Tables 1 and 2 and Fig. 1 and 2. Though some variability is evident from year to year, site to site, and surface soil to subsoil, these data make it abundantly clear that the upper meter of the soil in the Jackson-Frazier wetland is saturated,

Table 2. Duration of saturation (Sat.) and reduction (Red.) from November to October for each year and averages for the entire measurement period from 1992 to 1996 at Sites JF1 and JF2.

	Depth									1992	-1996
Site		1992-1993		1993-1994		1994–1995		1995-1996		Total	Total
		Sat.	Red.	Sat.	Red.	Sat.	Red.	Sat.	Red.		Red.
	cm						% —				
JF1	25	77	75	81	71	80	77	90	93	82	80
JF1	50	77	80	81	20	80	69	90	93	82	73
JF1	100	88	98	62	59	72	77	96	93	82	86
JF2	25	75	78	91	87	82	74	90	93	83	82
JF2	50	80	73	91	71	82	67	90	93	85	77
JF2	100	71	43	71	20	74	46	90	82	77	52

almost continuously, for at least 9 mo of the year, essentially from November through July.

During the 4-yr period of measurement, we experienced two drier-than-average years (1993-1994) and two wetter-than-average years (1995–1996). During the dry years, the upper 50 cm of soil was saturated 70 to 80% of the time, but during 1996 this increased to 90% (Table 2). At the 100-cm depth, dry-year saturation ranged from 62 to 88%, centered on figures in the low 70s. In 1996, however, the soil at 100 cm was saturated 90 to 96% of the time, and we suspect that it remained saturated continuously even throughout the summer when we were not making regular measurements of water levels in piezometers. Continuity of saturation is best illustrated by the horizontal bars in the lower half of Fig. 1 and 2. Scale limitations in these figures preclude showing the one or two times each year when weekly measurements showed empty piezometers, but in no case did we ever see unsaturated conditions for two consecutive weeks during the rainy season. The only proper conclusion from these data is that these soils are saturated nearly continuously throughout the late fall, winter, and spring, and that the cumulative effect of saturation is more than enough to produce anaerobic and reducing conditions, as data to follow will show.

Given the Xeric soil moisture regime, and the fact that these surface soils do become desaturated during late summer and early fall, we were interested in the lag time between the onset of rains in the fall and the redevelopment of saturated soil conditions. Because of seasonal variation, we have expressed the lag time data in Table 1 not in terms of number of days, but in terms of amount of rainfall needed before the soil becomes saturated. Disregarding the data from 1994, a year in which we did not begin field measurements until well after the rainy season had begun, the amount of rain needed to achieve saturation only ranged from 3.4 to 12.3 cm, with an overall average of 8.3 cm. There is a hint in the data that less rain was required in the dry years than in the wet years, a result that runs counter to intuition. If this is a real effect, then we would attribute it to the presence in dry soil years of wide, open cracks that allow virtually all of the early rains to infiltrate,

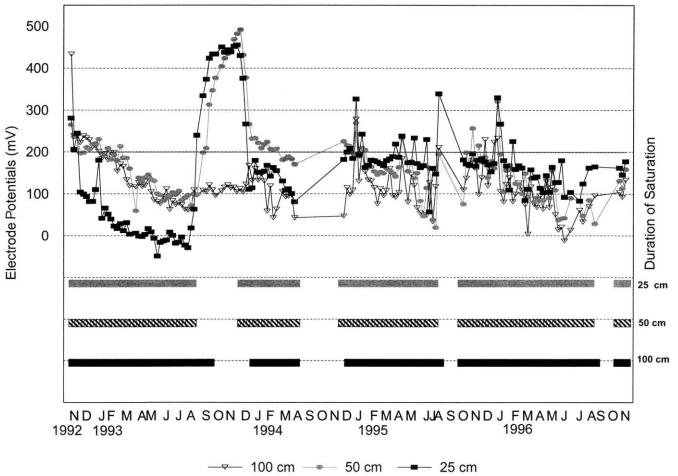


Fig. 1. Duration of saturation (bottom) and electrode potentials (top) at depths of 100, 50, and 25 cm at Site JF1.

whereas in the wetter soil years, earlier swelling and reduction of infiltration rates leads to more rapid ponding and runoff of hydrologic inputs, thus increasing the amount of rain needed to finally resaturate the surface soil.

Soil stratigraphy has a major impact on patterns of wetting. D'Amore et al. (2000) have established that the Jackson-Frazier soils become saturated from the top down in the upper Holocene alluvium and from the bottom up in the lower Irish Bend silts. Deep cracking in the high shrink-swell clays of the surficial unit allow rapid entry of water and nearly uniform development of saturated conditions, particularly in the upper 50 cm. Patterns of saturation and desaturation at 100 cm, however, are more dependent on stratigraphic differences. At site JF1, the 100-cm piezometer was installed near the base of the clayey Holocene alluvium, whose very slow permeability resulted in maintenance of saturated conditions late in the summer, even after the surface soil had become desaturated. At site JF2, the 100-cm piezometers were installed near the boundary of the 2Bt clay and the 3BC Irish Bend silts. Here, saturation occurred as the water table rose in the Irish Bend unit, and since this unit is much more permeable than the Holocene alluvium, water tables fell and the soil at 100 cm became desaturated earlier in the summer than at JF1.

Anaerobic conditions in saturated soil are documented with data on DO content of water in the piezometers (Fig. 3, 4). Variability in the data precludes absolute conclusions, but there are some interesting trends. First, DO levels tend to be higher in dry years than in wet years. Second, DO levels at 50 cm are almost always lower than DO levels at 25 cm, perhaps because of the influence of more oxygen-laden water entering the surface soil. Third, DO levels at both 25 and 50 cm are almost always  $\leq 2$  mg  $L^{-1}$ , and for much of the time in the wet years they are  $\leq 1$  mg  $L^{-1}$ . We think these values are low enough to indicate that the soil is essentially anaerobic. Fourth, DO levels at 200 cm, a depth well within the Irish Bend silts, are generally higher and more variable. We think this may be partly because of oxygen brought into the silts in groundwater flowing through the lower aquifer from a source area that allows for oxygen enrichment, and partly because of lower amounts of organic carbon, and hence less biological activity to deplete the supply of DO at this depth.

#### **Carbon and Temperature**

At both sites, the surface horizons to a depth of 16 to 18 cm average much more than 4% organic carbon (Table 3). The Bss horizons in the remainder of the Holocene alluvium average >1% organic carbon. Dark

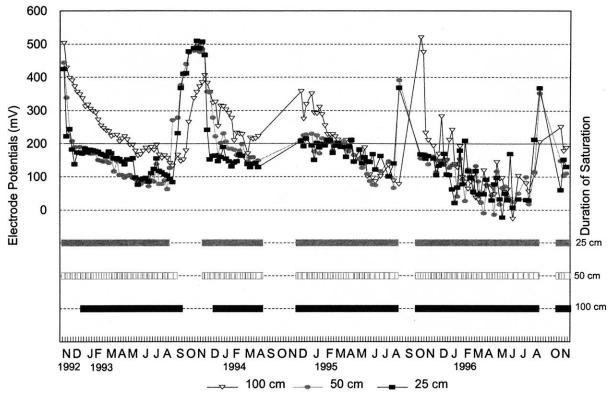


Fig. 2. Duration of saturation (bottom) and electrode potentials (top) at depths of 100, 50, and 25 cm at Site JF2.

colors throughout, particularly the 2/1, 2/0, and 3/0 colors in the Bss (Table 3), suggest that organic carbon is uniformly distributed and occurs as coatings on surfaces of clay particles. Though lacking direct evidence, we are confident that the carbon present throughout the entire Holocene alluvium provides a readily available energy source in amounts sufficient to support large popula-

tions of facultative and obligate anaerobes needed to mediate reduction processes in the soil.

Carbon contents are much lower in the 2Bt and 3BC horizons, averaging about 0.2 and 0.1%, respectively. We would expect carbon contents this low to be more limiting to microbial activity, yet the presence of redoximorphic features in both these horizons (Tables 3 and 4)

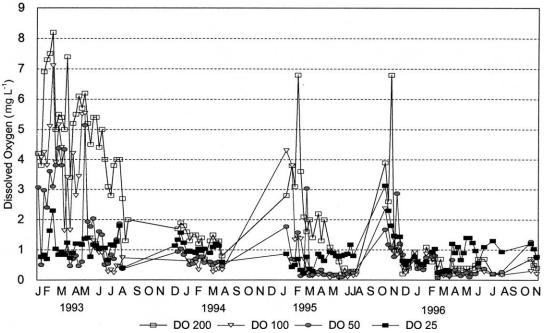


Fig. 3. Dissolved oxygen (DO) in piezometer water at depths of 200, 100, 50, and 25 cm at Site JF1.

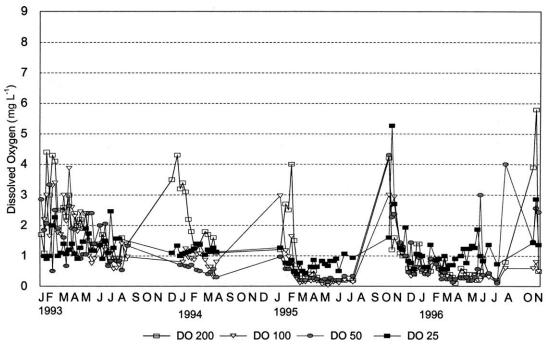


Fig. 4. Dissolved oxygen (DO) in piezometer water at depths of 200, 100, 50, and 25 cm at Site JF2.

suggest there is, or has been, enough oxidation of carbon to cause reduction of both Fe and Mn.

Soil temperatures rarely drop below 5°C, and when they do it is for very short periods of time (Fig. 5). Measurements nearest the surface, at 25 cm, show the widest extremes in temperature, as expected, and although microbial activity undoubtedly slows when the temperature is below 5°C, we don't believe it ceases altogether, as microbial activity has been noted in much more extreme environments (Michaelson and Ping, 2003). More important, given that the soil is almost continuously saturated from November to July, there are long periods of time, especially in the spring, when the soil is wet, the temperature is warming, adequate carbon is avail-

able, and conditions are prime for reduction of Fe and Mn.

# Iron and Manganese

Neither redox depletions nor redox concentrations can form if the original soil matrix contains too little Fe and Mn to reduce, translocate, and concentrate by reoxidation. The presence of both depletions and concentrations (Table 3) provides the best evidence that there is, or has been, adequate amounts of Fe and Mn in Jackson-Frazier wetland soils to support reductimorphic processes. Further evidence is provided by the DCB data in Table 5, which show that Fe contents in nodules

Table 3. Morphological properties of soils described at three sites at the Jackson-Frazier wetland.

Site	Horizon	Depth	Moist color	Black Fe/Mn concretions†	Soft masses	Organic C	Slickenside
		cm				%	
JF1	<b>A1</b>	0-8	10YR 3/2	_	_	7.98	_
JF1	<b>A2</b>	9-16	10YR 3/1	1f	1fp 7.5YR 5/6	3.42	_
JF1	A3	15-41	10YR 2/1	1f	1fd 7.5YR 5/4	1.32	1d
JF1	Bss1	41–66	60% 10YR 2/1 40% 10YR 4/2	<b>2f</b>	_	1.1	<b>3</b> p
JF1	Bss2	66–104	60% 10YR 4/2 40% 10YR 2/1	-	1fd 7.5YR 4/4	0.58	<b>3</b> p
JF1	2Bt1	104-119	2.5Y 4/2	_	1fd 7.5YR 4/4	0.22	_
JF1	2Bt2	119–135	2.5Y 5/2 2.5Y 4/2	_	1fd 7.5YR 4/4	0.15	-
JF1	3BC	135-155	2.5Y 4/4	-	-	0.08	-
JF2	<b>A1</b>	0-18	10YR 2/2	1m	_	4.56	_
JF2	Bss1	18-34	N 3/0	1m	1fd 5YR 4/4	1.36	2d
JF2	Bss2	34-50	N 2/0	2m	1fd 5YR 4/4	1.02	2d
JF2	Bss3	50-82	2.5Y 4/2 N 3/0	2m, 1c	_	0.73	<b>3</b> p
JF2	2Bt	82–100	2.5Y 5/3 N 3/0	1f, 1c	1fd 7.5YR 4/6	0.23	-
JF2	3BCt1	100-118	2.5Y 5/4	1m	2fd 7.5YR 6/4	0.12	_
JF2	3BCt2	118-140	2.5Y 4/2	1f (stains)	2fd 7.5YR 5/6	0.09	_

<sup>†</sup> Concretions, soft Fe masses, and slickenside abbreviations: 1 = few, 2 = common, 3 = many, f = fine, m = medium, c = coarse, d = distinct, p = prominent.

Table 4. Size range, mass, standard error for mass, density, and standard error for density of concretionary material in stratigraphic units at the Jackson-Frazier wetland.

Horizon	Size range	Mass	SE†	Density	SE‡	
	mm	mg kg $^{-1}  imes 10^2$	g cm <sup>-3</sup>			
Bss	< 0.5-12	169	6.2	2.1	0.10	
2Bt	< 0.5-7	77	2.9	2.1	0.08	
3BC	< 0.5-3	198	4.1	1.9	0.07	

<sup>†</sup> Standard error, n = 32.

and concretions are four to nine times as much as in their corresponding matrices, and Mn contents are even more markedly enriched, ranging from 23- to >500-fold increases. These data represent the amounts of extractable Fe and Mn currently present in both the nodule-free soil matrix and in the concretions and nodules themselves. Clearly, there has been enough Fe and Mn available to participate in redox reactions and concentrate into readily identifiable redoximorphic features.

# **Redox Potential Response to Field Conditions**

Responses of soil  $E_Hs$  to soil water status indicate that as the soil becomes saturated and anaerobic with the onset of the fall and winter rainy season,  $E_Hs$  drop quickly and remain at relatively low values ( $\approx$ 0 to 100 mV) as long as the soil remains saturated (Fig. 1, 2). In the spring, as rainfall diminishes and the soil desaturates,  $E_Hs$  rise above the threshold for Fe reduction (200 mV at pH 7) and remain there until the next rainy season begins.

After the fall rains begin, there is a lag time before the soil becomes saturated, and another lag time until the development of Fe-reducing conditions (Table 1). Note that 1992 and 1993 were relatively dry years, whereas 1995 and 1996 were unusually wet years. We do not show data for 1994 because we were unable to obtain water table and  $E_{\rm H}$  readings in the fall of 1994 until well after the soils had become saturated. During the drier years, it took on average about 2 wk after saturation for the soil at 25 cm to become reduced. The lag time increased with depth, ranging from 2 wk to 3 mo at 50 cm, and 2 to 4 mo at 100 cm. Once reducing conditions were reached, however, the soils tended to remain reduced until the soil became desaturated and aerobic again late in the spring.

In wet years, the lag time to reducing conditions was only a few days. Because field measurements were taken at weekly intervals, a zero entry in Table 1 means essentially that one week the soil was neither saturated nor reduced, and 7 d later it was both saturated and reduced. Thus, within those few days, the soil was presumably much wetter and already oxygen-deficient, and responded much more quickly to the final development of saturated conditions. This holds true at all depths, suggesting that even the soils at 100 cm, though unsaturated, must have remained very wet throughout the summer months.

Redox potentials in the surficial Holocence alluvium (Bss horizons) are represented by data from the 25- and 50-cm Pt electrodes at both sites. During the first 2 yr of

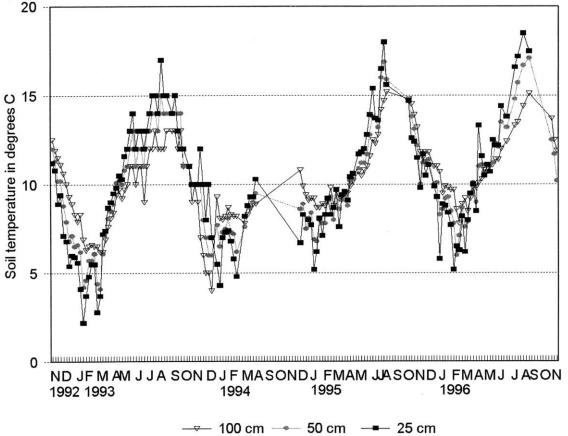


Fig. 5. Soil temperature data at depths of 100, 50, and 25 cm at Site JF1.

 $<sup>\</sup>ddagger$  Standard error, n = 6.

0.26

0.67

0.37

0.53

Fe Mn Ox/DCB Ox/DCB Horizon DCB† SE SE **DCB** SE Source Ox: SE Ox  $\rm mg~kg^{-1}~\times$  $10^{2}$ mg kg $^{-1} imes 10^2$ Bss matrix 233 0.13 16 1.0 14 0.0 0.88 small 2049 163 388 20.5 0.19 37.6 47 51 2.6 0.14 1661 162 337 17.3 0.20 77.8 103 183 3.8 0.24 large 2Bt matrix 184 15 0.9 0.08 1.0 0.0 1.0 0.0 1.00 1476 242 297 small 0.20

0.25

0.11

0.30

0.45

568

109

3.0

105

0.0

4.2

146

83

2.0

5.0

0.0

3.0

13.9

0.6

1.9

6.4

Table 5. Iron and Mn extracted from the soil matrix, small nodules (<2 mm), and large nodules (>2 mm).

370

22

294

large

small

matrix

1486

208

855

56

7

77

3BC

observations at JF1, E<sub>H</sub> values at 25 cm were consistently lower than E<sub>H</sub> values at 50 cm (Fig. 1). One might expect that, because the organic carbon content is higher near the surface, and in these two drier-than-normal years the soil forms wide cracks to at least 25 cm, biological activity is higher at 25 cm, and when the soil did become saturated and anaerobic, E<sub>H</sub>s quickly plummeted to low levels (≈100 mV). This is not a particularly convincing argument, however, given that the organic C contents at 25 and 50 cm are not very different (Table 3); that when the soils were dry and cracked, the cracks extended to about 50 cm; and that E<sub>H</sub> behavior at 25 and 50 cm was essentially the same in the two wet years at JF1 and throughout all 4 yr of observation at JF2 (Fig. 2). Soil cracking and the subsequent development of macropores (Bronswijk et al., 1993; Dziejowski et al., 1997) and pore connectivity (Ritchie et al., 1972; Zausig et al., 1993) have been shown to influence oxygen diffusion in soils. Undoubtedly, these processes lead to a complicated system where the shrink-and-swell clay of the Vertisols creates a complex, dynamic pore-size distribution. The important conclusion from these data is that, despite some unexplained variation, E<sub>H</sub>s in the Holocene alluvium respond decisively to conditions of saturation and anaerobiosis and document the persistence of an environment conducive to the reduction of Fe throughout the duration of saturated conditions.

Two other trends in the data are worth noting. One, E<sub>H</sub>s at all depths at both sites continue to decline throughout the period of saturation and reach their lowest levels (≈0–100 mV) just before desaturation and the return of aerobic conditions. These data make it clear that the longer continuous or nearly continuous saturated conditions persist, the more strongly reducing the soil becomes. Two, there's more variability in the E<sub>H</sub> readings in the latter part of the study, particularly in Year 4. Changes in microsite variability from cumulative effects of wetting and drying (Sextone et al., 1985; Jacob et al., 1997), shrinking and swelling (Hodgson and Macleod, 1989; Jacob et al., 1997), and length of intervals between rain events all could be factors in increasing variability. It is also possible that this is an instrumental effect, indicating that the electrodes are becoming less reliable the longer they remain in the soil, despite the demonstrated viability of permanently installed Pt electrodes (Austin and Huddleston, 1999).

Redox potentials at 100 cm exhibit different behaviors from JF1 to JF2. At JF1, the 100-cm electrode is at the base of the Holocene alluvium, immediately underlain by Malpass clay (2Bt horizon). At JF2, the 100-cm electrode is at the base of the Malpass clay, immediately underlain by Irish Bend silts (3BC horizon). Redox potentials at JF1 are generally lower than at JF2 (0-100 vs. 100–150 mV), reflecting earlier onset and longer duration of saturation. Redox potentials at JF2 appear to be influenced by hydrological and DO conditions in the Irish Bend silts, which become saturated later in the year and for shorter durations, particularly during dry years (Fig. 2), in which DO levels are considerably higher at the onset of saturation than in the more clayey units above (Fig. 4).

#### **Formation of Redoximorphic Features**

All the data we have presented provide firm evidence that current conditions are favorable for the formation of redoximorphic features in each of the three major stratigraphic units that underlie the Jackson-Frazier wetland. Data in Table 3 show that redox features are present in each unit. Remaining questions of interest include differences in amounts and kinds of features from unit to unit and whether features are currently forming or simply reside unchanged in an environment that is still conducive to their formation.

Two kinds of redox features are present within the Jackson-Frazier soils: black Fe/Mn nodules and concretions, and high chroma soft masses of Fe accumulation. Our primary interest is in the nodules and concretions, since these are particularly characteristic of poorly drained soils in the Willamette Valley (Drosdoff and Nikiforoff, 1940; Parsons and Balster, 1967; Somera, 1967; Boersma et al., 1972; Seter and Baham, 1994). Soft masses provide further insight into translocations of Fe and Mn within and between stratigraphic units.

Physical characterization data for nodular material in each stratigraphic unit are shown in Table 4. Chemical characterization of the more crystalline (DCB-extractable) and the more poorly crystalline (oxalate-extractable) Fe and Mn oxides are shown in Table 5. As we interpret these data, bear in mind that groundwater rises and falls seasonally within the lowermost Irish Bend silts, surface water enters cracks and saturates the upper-

large † DCB = dithionite citrate bicarbonate.

 $<sup>\</sup>pm Ox = oxalate$ .

most Holocene alluvium from the top down, and the Malpass clay in the middle becomes saturated both from the bottom up and the top down, and remains saturated or very wet for longer periods of time than either the underlying or the overlying strata (D'Amore et al., 2000).

The deepest and oldest stratigraphic unit, the 3BC Irish Bend silts, contains the greatest mass of nodular material (Table 4). These nodules, however, are on average smaller and more numerous than those found in both overlying stratigraphic units. The evidence is indirect, as we do not have absolute counts of nodules in various size classes. But the maximum nodule size in this unit is only 3 mm, compared with 7 and 12 mm in overlying units, and the number of nodules per unit area in the 3BC is lower, thus there must be a greater quantity of small nodules to account for the higher mass (Table 4).

Microscopic examination of 3BC nodules revealed an irregular, botryoidal shape, in contrast to the more nearly spherical shape of concentrations in the 2Bt and Bss horizons. Chemical data (Table 5) show that 3BC nodules have lower concentrations of Fe and Mn oxides than the nodules in the 2Bt above. Taken together, these two lines of evidence suggest that the 3BC concentrations are nodules in the true sense of the word, that is, they have formed by precipitation of Fe and Mn oxides in tiny pores, surrounding and embedding grains of the matrix soil to form a nodule. The fact that the 3BC nodules are a little less dense than the concretions in the 2Bt and Bss horizons supports this conclusion.

Chemical and morphological data also suggest that the 3BC nodules are currently forming in the soil. First, although many nodules appear to have sharp boundaries with the matrix, some do have diffuse halos of soft Fe accumulation, evidence that is considered indicative of current formation (Vepraskas, 1994). Second, 3BC matrix chromas from two to four suggest that there remains in the soil a source of Fe that can be reduced, translocated, and concentrated in nodular form. Indeed, the data in Table 5 show that, whereas the extractable Mn is virtually gone, there remains both DCB- and oxalateextractable Fe as potential sources for continuing Fe mobilization and concentration. Third, the ratio of oxalate Fe to DCB Fe increases from 0.30 in the small nodules to 0.45 in the large nodules; apparently, nodules are currently growing by continuing accretion of the more poorly crystalline forms of Fe.

We postulate a 3BC nodule formation model in which both the more crystalline, DCB-extractable Fe and the more poorly crystalline, oxalate-extractable Fe can be reduced and mobilized by redox processes in the soil. Early in the process of nodule formation, mobilized Fe is translocated to small pores where it reoxidizes as very poorly crystalline Fe deposits. As these initial Fe deposits age, much of the Fe may be reorganized into more crystalline forms as the Fe minerals themselves dehydrate. Conversely, continued growth of the nodule adds incremental amounts of more poorly crystalline Fe to the volume of the nodule, which causes the Fe<sub>Ox</sub>/Fe<sub>DCB</sub> ratio within the nodule to increase. Thus, although the more crystalline Fe pool increases with age, the ratio of poorly crystalline Fe to more crystalline Fe increases

due to nodule geometry. That we see such a relatively high  $Fe_{Ox}/Fe_{DCB}$  ratio in the large 3BC nodules suggests that growth is contemporary. Thus, we believe that the 3BC nodules are forming in the contemporary soil environment, and they will continue to do so as long as there is an adequate supply of reducible Fe in the 3BC matrix.

The 2Bt is very different. Iron–manganese concentrations are generally spherical, denser, and contain more Fe and Mn than nodules in the 3BC. Scanning electron microprobe analysis (data not presented) showed relative concentrations of Mn in the center regions and of Fe in outer regions. These concentrations look very much like true concretions, and we believe they are. Most of these concretions have sharp boundaries, with the larger ones up to 7 mm in diameter. The total mass of concretionary material, however, is less than half as much as found in both the 3BC below and the Bss above (Table 4). Thus, we find the least amount of concretionary mass in that part of the soil that remains saturated the longest, a result that agrees with earlier observations of Arshad and St. Arnaud (1980) and Rhoton et al. (1993). These results also support the work of Schwertmann and Fanning (1976) and Richardson and Hole (1979), who observed that optimal concretion formation is often found in areas of fluctuating water tables, rather than areas of more permanent saturation.

Color chromas of the 2Bt matrix are dominantly two or less (Table 3). Extractable Mn is virtually absent, and extractable Fe contents are lower than in either the 3BC or Bss (Table 5). A small amount of oxalateextractable Fe remains, and the widening of the  $Fe_{Ox}$ Fe<sub>DCB</sub> ratio from small to large nodules, combined with the fact that we do see a few concretions that have diffuse halos, suggest that some accretionary growth of nodules may still be taking place today. The weight of the evidence, however, points to almost complete exhaustion of the supply of Fe and Mn available to be reduced, translocated, and concentrated. This is consistent with the loss of Fe and Mn in nearly permanently saturated soils (Blume, 1988). Thus, the concretions we see in the 2Bt formed primarily at an earlier time and now simply reside, mostly unchanged, in an environment that would still be conducive to their formation if any Fe and Mn were left in the matrix to redistribute.

Given that there are fewer nodules in the 2Bt and less Fe and Mn remaining in the 2Bt matrix than in units above and below, where did all the Fe and Mn go? One possibility is that the Malpass clay simply contained lower amounts of Fe and Mn when it was deposited about 15 000 yr ago. We can't test that hypothesis because we can't obtain a sample of the original deposit that has not been altered by redox processes in the intervening millennia. Another possibility is that some Fe and Mn have been lost by leaching. Recall that the 2Bt remains wetter and reducing longer than the other units. Despite slow permeability, across time some soil water could leak out the bottom of the 2Bt, especially after the water table in the 3BC had dropped, creating an aerobic zone at the top of the 3BC. Redox concentrations in the form of high chroma soft masses observed in the upper part of the 3BC at site JF2 provide some

support for the theory that reduced Fe coming out of the 2Bt was oxidized and precipitated in the higher E<sub>H</sub> environment of the upper 3BC. This has been observed in other soils where finer-textured soil overlies a coarser-textured horizon (Veneman et al., 1976; Clothier et al., 1978).

Concretionary material in the Bss is physically and chemically similar to that in the 2Bt, except that a greater proportion of the Bss concretions have soft Fe halos in proximity to them. Data for the Bss matrix (Table 5) show that there is more of every form of extractable Fe and Mn than in both lower stratigraphic units and suggest that there is still plenty of Fe and Mn available for redistribution. This is not a surprising result, as continuing deposition of the Holocene alluvium, which is derived from Fe-rich soils and rocks at the headwaters of Jackson and Frazier creeks (Snavely et al., 1968; Glasmann and Simonson, 1985), provides fresh Fe for concretion formation. Nearly identical values for Fe<sub>Ox</sub>/Fe<sub>DCB</sub> ratios for both large and small concretions imply that DCB-extractable-only Fe is still accreting, along with oxalate-extractable Fe and both forms of extractable Mn. Perhaps this fact explains why some of the concretions observed in the Bss are relatively very large—up to 12 mm in diameter.

All the evidence points to contemporary formation of Fe/Mn concretions in the Bss. One final piece of evidence confirms this hypothesis. X-ray mineralogical analyses revealed that soil nodules from upland soils from which the sediments ultimately deposited in the Jackson-Frazier wetland were derived, were rich in kaolinite, goethite, maghematite, and hematite. However, Bss nodules contained mica, vermiculite, kaolinite, smectite, and some goethite, purpurite, and manganite (Stewart, 1997). Upland soil nodules also were much harder and could not be fractured in the hand. The differences between these two sets of nodules are so striking that we conclude the presence of concretions with sharp boundaries in the Bss matrix does not mean that these nodules were transported with the alluvium, but have been and are still forming in place under contemporary redox environments.

The data in Table 4 allow us to estimate general rates of nodule and concretion formation. Taking as reasonable estimates of the ages of each stratigraphic unit, 3 ka for the Holocene alluvium, 15 ka for the Malpass clay, and 50 ka for the Irish Bend silts (Reckendorf, 1993), we calculate nodule formation rates, in dg kg<sup>-1</sup> ka<sup>-1</sup>, of 0.56 for the Bss, 0.05 for the 2Bt, and 0.04 for the 3BC. The relatively high rate of formation in the Bss reflects the facts of contemporary formation in an environment that undergoes prolonged periods of saturation and anaerobiosis, has an abundance of Fe and Mn to redistribute, and has plenty of carbon to facilitate reduction of Fe and Mn. Whether the initial rates of formation in the 2Bt ever approached the rate calculated for the Bss we simply don't know, but it's clear that the contemporary rate is very slow, approaching zero, so the calculated rate must represent a long-term average across a rate curve that has been decreasing steadily, but probably not linearly, with time. Similarly, we have no way of knowing what the initial rates of nodule formation in the 3BC might have been, but given the conditions of seasonally fluctuating redox conditions, continued presence of some reducible Fe, low amounts of organic carbon, and evidence of contemporary nodule formation, the pattern suggests more of a slow but steady and continuous mode of nodule formation. Still, nearly all of the extractable Mn and some of the Fe is gone, so contemporary rates of formation in the 3BC must be somewhat less than initial rates.

#### **CONCLUSIONS**

Geological events associated with Late Pleistocene flooding and Holocene erosion and sedimentation have had a marked effect on the hydrological behavior of the Jackson-Frazier wetland. Under contemporary climatic conditions, the wetland becomes saturated and anaerobic in each of the three major stratigraphic units present, although the seasonal duration of such conditions varies from unit to unit and year to year. Supplies of organic carbon are high in the surficial stratigraphic unit and low in underlying units, yet in all three the supplies are adequate to cause  $E_{\rm HS}$  to fall into the range of Fe reduction for long periods of time during most years.

Redox concentrations in the form of Fe–Mn nodules, concretions, and soft masses are present in each stratigraphic unit, and data on the amounts of extractable Fe and Mn document substantial depletions of these constituents from the matrix soil in all three units. Extractable Mn is virtually gone from the two older units, and there is evidence that almost all of the reducible Fe also has been removed from the matrix of the middle stratigraphic unit, the 2Bt Malpass clay. In this unit, the vast majority of the redox concentrations are spherical concretions with sharp boundaries. We conclude they have formed in place, but they are no longer actively growing by accretion of Fe and Mn because the source supply in the matrix has been exhausted. They are not, however, relict features (Hurt et al., 2002) because they still do reflect current hydrologic conditions of saturation and anaerobiosis.

Below, in the 3BC Irish Bend unit, irregularly shaped nodules rather than concretions have formed as Fe and Mn have crystallized in small pores, surrounding and embedding grains of matrix soil as they grow. We think that nodule formation is favored over concretion formation in the 3BC because the silt loam texture favors a pore structure that provides microsites for reoxidation of reduced Fe and Mn as they drain and become aerobic seasonally. Further, the low carbon content favors slow rates of formation, and the wider ratio of oxalate to DCB Fe in large nodules suggests that these nodules are still growing in today's hydrological environment.

The surficial stratigraphic unit, the Bss Holocene alluvium, is young enough to still contain adequate supplies of reducible Fe and Mn. Carbon contents are also high, and the soil quickly becomes anaerobic with the onset of saturated conditions at the beginning of the rainy season. The combination of all of these factors results in the rapid formation of redox concretions, some of which

are growing to sizes larger than observed in either of the two lower units. Diffuse boundaries, though not present around all concretions, indicate formation in place, a conclusion that is substantiated by mineralogical data that show wide differences between concretions in the alluvium and nodules in the upland soils from which the alluvium was derived.

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